Structure of High and Low Temperature Phases and Their Relationship With Oxygen Deficiency in $Li_{1+y}Mn_{2-y}O_4$ Type Cathode Materials

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Introduction: It was discovered by Yamada and Tanaka[1] in 1995 that stoichiometric $LiMn_2O_4$ undergoes a structural first order phase transition from a cubic (Fd3m) to a tetragonal ($I4_1$ /amd) structure at a temperature about 280 K during cooling. They also concluded that the mass fraction of the tetragonal phase increase with decreasing temperature, but saturated to a value of 65% below 260 K. Using x-ray diffraction (XRD), neutron diffraction, and electron diffraction data collected at different temperatures, Oikawa[2] proposed a low temperature phase with orthorhombic symmetry (Fddd) and claimed that the mass fraction of (Fddd) phase is close to 100% at temperature below 250 K. More recently, Rodriguez-Carvajal[3] proposed a partial charge ordering of Mn^{3+} and Mn^{4+} model for this phase transition. The symmetry of the low temperature phase was assigned as orthorhombic (Fddd) with a larger unit cell selected ($3a \times 3a \times a$ super cell). They also claimed that only single orthorhombic phase exists at 230 K. In almost every published reference, the origin of this phase transition has been attributed to the Jahn-Teller distortion, and the average oxidation state of Mn has been considered as the most important factor for this phase transition. However, in a related topic, the oxygen stoichiometric effects on structure and lithium insertion in $LiMn_2O_4$ have also been discussed by several research groups[4,5,6,7,8] . Based on our differential scanning calorimetry (DSC) and *in situ* XRD data, we believe that the key factor for the phase transition is the population of oxygen vacancy, the transition is due to oxygen vacancy ordering.

Methods and Materials: A series of $Li_{1+y}Mn_{2-y}O_{4-z}$ type (y=-0.05, -0.02, 0, 0.04, 0.06, and 0.10) cathode materials have been synthesized by a solid state reaction. The oxygen contents of these materials were controlled by varying the reaction temperature and the atmosphere (under O_2 or N_2). *In situ* XRD spectra were collected at an energy of 10375 eV (λ=1.195 Å)

Results: Differential Scanning Calorimetry (DSC) studies show that both the temperature and the integrated area of exothermic peak associated with the phase transition from the high temperature phase to low temperature phase are increased with increasing degree of oxygen deficiency. The *in situ* x-ray diffraction spectra collected at every 5 degrees on the oxygen deficient sample when cooled from 25 °C to –60 °C show that the structure of low temperature phase has tetragonal symmetry. After cooled to –60 °C and kept the temperature at –60 °C for more than 2 hours, more than 30% of the material was still not transformed from the cubic phase to the tetragonal phase. These results are consistent with the original observation of Yamada and Tanaka. The *in situ* x-ray diffraction spectra collected on a series samples with different level of oxygen deficiency show that the percentage of tetragonal phase is proportional to the degree of oxygen deficiency. In other words, the higher the population the oxygen vacancy, the higher the percentage of the tetragonal phase at –60 °C. These results are consistent with our DSC data. Therefore, we believe that the origin of this phase transition is due to the ordering of oxygen vacancy, not the ordering of Mn^{3+} and Mn^{4+}. When the battery cell using oxygen deficient $LiMn_2O_4$ as cathode was charged from 3.5 to 4.5 V at 0° C, *in situ* XRD spectra show that the low temperature tetragonal phase is converted to regular cubic spinel structure during charge.

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